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(54) Title: ELECTRICALLY HEATABLE, TRANSPARENT WINDOWS AND MIRRORS AND METHOD FOR PRODUCTION

(57) Abstract

Materials and processes are disclosed for the printing of invisibly thin silver lines on windows and mirrors to allow them to be electrically defrosted or demisted. The lines are so thin that they are not visible, providing completely transparent windows or mirrors to the eye and uniform moisture removal, unlike currently used electrical defrosting means.

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Electrically Heatable, Transparent Windows And Mirrors And Method For Production

Background of the Invention

In winter seasons or cold areas, deposition of snow, ice, frost, or moisture or the like takes place on the glass surfaces of vehicles, such as, trains, trucks, and passenger cars, as well as the window glass of buildings hindering visibility. As an example, automotive glass has traditionally been defrosted using forced air heating ducts or electrically conductive paint, such as silver paint, printed as gridlines fused onto the glass. The silver conductors commonly used on back windows would not be suitable for windshields because the heater traces are approximately one millimeter wide, and are quite noticeable and distracting. Another drawback of these traces is that they do not heat the back light uniformly, resulting in stripes of clear glass with ice or moisture between them.

Yet another method currently used is to apply a conductive transparent film the glass or to incorporate an electrical conductor in between laminated glass layers. Examples of such electrical conductors include heating wires made of tungsten or molybdenum, films of transparent conductive oxides such as ITO (tin doped indium oxide) layers and a thin silver coating. While silver layers can be thin enough to be fairly transparent to visible light, they are also conductive enough to provide adequate ohmic heating for defrosting. Use of a silver coating in automotive windshields, however, is less than desirable because it requires special fabrication techniques. The optical and electrical properties of the silver layer may degrade at the elevated temperatures employed for bending glass, approximately 600 °C for 10 minutes. Thus such silver coatings had to be applied after bending of the glass was completed. In addition, since a transparent film of silver is itself not particularly durable, its usefulness was limited to areas where it was protected, such as inside the laminate of the windshield. Even then additional layers were added to protect the silver layer and improve its optical performance.

A superior solution to this problem would be to produce much finer printed conductors which could be placed much closer together to obtain uniform heating, and which would be so narrow that they could not be seen.

Transparent electroconductive windows having ceramic silver bus bars making electrical contact with a transparent electroconductive coating are disclosed in many patents, including U.S. Pat. Nos. 2,710,900 to Linder and 2,724,658 to Lytle.

U.S. Pat. No. 2,813,960 to Egle et al and 3,440,408 to Brittan disclose laminated glass assemblies in which thin wire is used as the heating element. Despite these patents, a need still existed for a bus bar material that is relatively easy to apply and when applied would make a good, permanent electroconductive contact with the elongated wire elements carried by the interlayer material of a laminated window.

U.S. Pat. No. 3,469,015 to Warren discloses a bus bar of a silver paste consisting of silver flake and a binder resin disposed in a groove in a glass substrate.

U.S. Pat. No. 3,553,833 to Jochim et al discloses bus bars comprising silver strips attached to a glass base by soldering. The attached strips are a suspension of silver and lead borosilicate in an organic base which evaporates upon heating.

U.S. Pat. No. 3,623,906 to Akeyoshi et al discloses bus bars formed of solder applied using a soldering spatula whose tip is at 350.degree. C. during the bus bar application.

The above-identified patents either provide bus bars having a non-electroconductive component (organic binder or ceramic frit), bus bars that are applied at elevated temperatures above those usually used in laminating, or bus bars that are applied in the solid state.

International Publication Number WO 98/37133 published August 27, 1988 and U.S. Patent 5,882,722 issued on March 16, 1999 to Kydd, which is incorporated herein by reference, disclose compounds containing a Reactive Organic Medium (ROM) and metal flakes and/or metal powders. The ROM consists of either a Metallo-Organic Decomposition (MOD) compound or an organic reagent, which can form such a compound upon heating in the presence of the metal constituents. The ingredients are formulated to produce printing inks or toners for electrostatic printing. These inks and toners can be printed on a substrate, such as plastic or glass, and thermally cured to well-consolidated, well-bonded electrical conductors at low temperatures.

Detailed Description of the Invention

PARMOD™ compositions can be printed in fine detail. When printed in extremely fine lines, 25 micrometers or less in width, the lines cannot be seen with the naked eye. This makes possible construction of electrically heated windows or mirrors on which the heating elements are invisible. Such windows and mirrors can find use on automobiles and buildings, for example.

The basis of PARMOD™ technology is that mixtures of Metallo-Organic Decomposition (MOD) compounds and metal powders can be applied directly to conventional polymer-based substrates by any convenient printing technology and heated to decompose them to well-bonded, well-consolidated pure metal. A basic disclosure of PARMOD™ technology can be found in PCT Patent Application, Serial No. WO 98/37133 published 27 August 1998. MOD compounds are those in which the metal is bound to the organic moiety via a heteroatom constituting a weak bond. While O, N, S, and P can serve as the heteroatom, preferred MOD compounds are metal soaps of carboxylic acids with oxygen as the heteroatom. The decomposition process occurs at temperatures of about 200-250°C for silver. This is low enough to be compatible with many substrates, including for example glass, polycarbonates, acrylic esters, polyesters, polyvinyl acetals, polyurethanes, and heat sensitive polymer substrates. PARMOD™ materials have been applied by screen printing, stenciling, gravure printing, electrostatic printing and ink jet printing. This PARMOD™ technology, based on MOD coated metal particles, can be used to formulate liquid toners useful in electrostatic printing. These toners can be used to print high resolution images which can be converted to pure metal conductor traces of high electrical conductivity.

Parmod™ silver lines ten micrometers wide, one micrometer thick and 50 cm long will have an electrical resistance of 850 ohms. If the lines are spaced on millimeter apart and connected to a twelve-Volt supply, they will dissipate 338 Watts per m². This is a reasonable 20-ampere load for an average sized rear window.

Normally patterns of heater traces consist of parallel lines. In the case of these ultrafine lines it may be advantageous to print the pattern as a mesh of interconnected lines.

In this way if a single line is defective or is broken in service, there is an alternate path for the current and the defect is localized. A rectangular grid or a hexagonal pattern like chicken wire would be suitable. The traces are connected to an electrical energy source by means well known in the art, such as bus bars – commonly used in the automotive industry. Using PARMOD™ technology the traces and the bus bar could be printed and cured at the same time.

Such an array can be produced by printing Parmod™ lines on glass and heating it to a minimum of 260°C for a minute or more to bond it to the glass. The normal processing temperature of curved glass panels is higher than this, and the times are much longer. These conditions will be more than adequate to convert the Parmod™ to pure, well-bonded silver traces.

The traces can be printed directly on the glass substrate and cured or, in another embodiment, the traces are printed and cured on a plastic substrate, and the plastic substrate is then placed between layers of a laminated glass or windshield. Using PARMOD compositions, which cure at low temperatures makes the use of many possible plastic substrates possible.

Very fine lines can be produced by gravure printing and by pad printing. In the first case a plate is made by etching or photoprocessing to produce a series of very fine grooves. The grooves are filled with ink, and the plate is pressed against the substrate to transfer the pattern of lines to the substrate. Currency and financial instruments of all kinds are examples of gravure printing. Lines 25 microns wide are readily produced in this way.

In pad printing and in related flexographic printing, a pad is patterned with an array of fine lines much like a rubber stamp pad, but much finer. The pad is inked and pressed on the substrate to transfer the lines to the substrate. Pad printing is used on curved, non-porous surfaces.

A preferred process for producing extremely fine lines is electrostatic printing, analogous to laser printing or xerographic copying. In this case, an image is created by

electrostatically charging an exposed photoreceptor which creates an electrostatic latent image. This image can be developed by exposing it to a toner containing charged particles.

The toned image can be transferred to the final substrate electrostatically. Glass sheets lend themselves to this transfer printing process because they are flat and smooth to a high degree, and because glass is an excellent electrical insulator. The glass is suspended above the toned image on the photoreceptor and charged by passing a corona discharge over the upper surface. The charge attracts the toner to the glass surface and holds it there until it can be cured to pure metal by heating the glass.

Yet another method for producing the latent charged image is to write it directly on a glass or plastic substrate with a high-energy electron or ion beam. If the glass sheet is passed beneath a source of focussed electrons or ions with an energy of 100,000 Volts or more the charged particles will be embedded in the glass in a very fine pattern which can be used to attract toner particles to create fine conductor lines. Electrons can pass through a window from the high voltage source and through a modes air gap without significant losses or defocusing. An electron beam may allow the patterning to be done in air at high speed rather than in vacuum, thereby substantially lowering costs.

Still another way to produce the charged latent image is to print it on a special substrate using a line of discharge electrodes which are pulsed to high voltage to deposit a pattern of electric charge on the substrate directly. Examples of such printers are manufactured by Raster Graphics, CalComp, and Phoenix Precision Graphics. The special substrates consist of an insulating polymer surface approximately 10 micrometers thick on a somewhat conductive paper backing. These printers typically print a meter wide web which is suitable for printing a heating pattern on a polymer layer to be laminated between glass or plastic sheets.

A preferred electrostatic process of this invention consists of the following steps:

- 1) An electrically conductive substrate is coated with a photoresist material, either in dry film or liquid form.
- 2.) The photoresist is imaged with a negative phototool of the electrical circuitry which is desired.

- 3.) The photoresist is cured to crosslink the exposed areas.
- 4.) The cross-linked latent image is charged by exposure to a corona discharge of the appropriate polarity for the liquid toner to be applied.
- 5.) The charged image is flooded with a liquid metallic toner suspension to create a physical image of the final device.
- 6.) The physical image is then transferred to a glass or plastic substrate and thermally cured to consolidate the toner material into a solid conductor or other component and to bond it to the substrate.

The method of this invention can be applied advantageously to create patterns of metal conductors on glass, plastic, or polymer surfaces. Any pattern can be applied, such as lines, grids, and hexagonal meshes.

The resist-coated substrate is preferably based on conventional printed wiring board laminates with a conductive surface, for example, copper foil attached to both sides of a glass-reinforced epoxy panel. The substrate is coated with a photosensitive resist material and exposed to light shining through a photographic negative of the desired final image. When the resist is cured, the image is crosslinked and rendered nonconductive electrically. A corona discharge will charge the image positively or negatively as desired, and the uncured area, which is more conductive than the cured photoresist, will dissipate the unwanted charge. A conductive ground plane, such as copper, under the resist is preferred to accomplish this dissipation.

The charged image is bathed with the liquid metallic toner suspension, and the charged toner particles are attracted to the oppositely charged image. The particles are then transferred to a separate dielectric substrate placed over the image and charged to attract the toner. The original image can be recharged and reused many times like a printing plate.

When a previously exposed and crosslinked resist-coated copper laminate was charged positively and bathed with the liquid metallic toner, a very high quality image was formed with good definition of fine features and good coverage of large solid areas. The image transfers well to a positively charged glass plate suspended above it

Electrostatic printing involves the use of a liquid toner to develop a latent electrostatic image. A latent electrostatic image is created by applying an electrostatic charge, via a corona, to a photoimaged layer of resist on a grounded substrate. The liquid metallic toner is then applied to the substrate to develop the image through the electrostatic attraction of the charged toner particles to the oppositely charged image areas. The toned image can then be transferred to a second substrate. The transfer is performed by placing the transfer substrate over the image on the grounded substrate using spacers to create a gap, which is filled with the dispersing solvent used in the liquid toner. The corona is again passed over the sample to provide an electrostatic transfer charge. Under the influence of the transfer charge, the toner is transferred through the dispersant filled gap to the second substrate. The image on the second substrate is then thermally cured to convert the toner to pure metal and maintain the image integrity.

The liquid metallic toner comprises metal particles combined with a functionalized metallo-organic compound dispersed in a non-polar organic medium. When a charge director is added to the dispersion, a charge is imparted to the metal particles, and the particles can be electrostatically printed, transferred, and cured to give a high resolution, well-consolidated, well-bonded metallic conductor on various substrates.

The three major components of PARMOD™ based liquid metallic toners are 1) metallic toner particles comprised of metal particles and metallo-organic decomposition (MOD) compound, 2) one or more charge director(s), and 3) a non-polar dispersing solvent. The MOD constituent of the toner particles is important because it interacts with the charge director(s) to impart a charge on the particles. The MOD, along with the charge director, can be used to vary the charge to mass ratio of the particles which is important to good electrostatic imaging. The MOD and the charge director also work in tandem to provide dispersability of the particles in the non-polar dispersing solvent. The MOD also allows for the PARMOD™ type consolidation of the metallic toner particles into a continuous metal film/conductor.

Metals which can be used as toner particles include copper, silver, gold, zinc, cadmium, palladium, iridium, ruthenium, osmium, rhodium, platinum, iron, cobalt, and nickel, (Groups Ib, IIb, and VIII), and manganese, indium, tin, antimony, lead, and bismuth

The MOD of the toner particles can be formed as the particles are being formed in a metal precipitation reaction. The metal precipitation reaction is performed by dissolving or suspending a metal salt in the MOD compound it is to be combined with, and heating the solution or suspension to decompose the metal salt to form metal particles. As the metal particles form, they will reach a certain particle size at which point the solvent (organic medium) will react with the surface forming a MOD coating on the particles, thus stabilizing them at that particle size. It is believed that this process not only coats the metal particles but that some of the MOD compound is also incorporated amongst the metal particles. The restraint on this reaction is that the metal salt chosen for decomposition must have a lower decomposition temperature than the coating "salt" formed on the surface of the particle. This process is similar to the process disclosed in U.S. Patents 4,186,244 & 4,463,030, both issued to Deffeyes. In one example the powder is made by thermally decomposing silver oxalate in a carboxylic acid (such as oleic acid). The resulting silver powder particles contain incorporated carboxylate and are effectively coated with the carboxylate.

When commercial metal particles are used, the MOD coating compound can be added to uncoated particles and adsorbed on the surface. This is accomplished by mixing the metal particle and the coating compound together in the dispersing medium. In the case of most metals, the coating compound will adsorb on the surface of the particles once mixed into the dispersing medium. This adsorption will give some amount of dispersability to the metal particles, depending on the coating compound used and its properties in the dispersing medium.

Preferred coating compounds are generally long chain carboxylic acids. The long organic chain provides dispersability in the dispersing solvent and the carboxylate functional group allows for strong adsorption on the metal particle surface. The functional group on the coating compound can be any ionizable group that would create an O, N, S, or P linkage with the metal particle surface. These types of linkages are important since the coating on the metal particles encompasses the PARMODTM technology and enables the consolidation of the particles into a continuous film. The organic part of the compound can be a long chain, a branched chain, or contain cyclic groups, as long as it has solubility or micellular properties

conductive to a non-polar organic solvent. The coatings on the metal particles that can be used include carboxylic acids, metal carboxylates, thiols, amines, alkoxides, and phosphines.

Commercially available metal powder or flake can be used and coated with silver neodecanoate. As an example, this is done by adding silver powder or flake to silver neodecanoate just after it has been synthesized and is still an 'oil'. The silver neodecanoate then forms a coating on the silver powder or flake. This 'oily' powder or flake can then be 'dried' (as the silver neodecanoate would be) by washing with methanol to give a dry powder.

The required charge control agents on the toners are preferably the MOD coatings on the metal particles. In general, a charge control agent must either be insoluble in the carrier solvent or be bound to the toner particle. It must be structurally capable of interacting with the charge director to generate the charge on the toner particle. Some examples of charge control agents are aluminum salts of organic acids, quaternary ammonium salts, and low molecular weight organic acids. Preferred charge control agents are carboxylic acids such as neodecanoic acid, neoheptanoic acid, neopentanoic acid, 2-ethylhexanoic acid, oleic acid, and silver neodecanoate.

The main function of the charge director is to provide the charge on the toner particles. As such, it also acts as a dispersing agent. The general properties of a charge director include its solubility in the carrier liquid, its ability to structurally interact with the charge control agent to provide the charge on the toner particle, and it should not be "very" hygroscopic. In general this means a molecule that contains an ionizable functional group as well as an organic portion which is soluble in the carrier solvent. In relation to the 'structural interaction with the charge control agent', the charge director's functional group should be able to interact ionically with the charge control agent, without being sterically inhibited by the organic portion.

The charge directors are thought to impart charge to the particles by forming inverse-micelles in the non-polar dispersing solvent. These inverse micelles then solubilize the ionic functional group of the organic coating compound, allowing ionization and the creation of a charge at the surface of the metal particle by proton transfer for example. By using a charge

director separate from the coating on the particle, it is possible to vary the amount of charge widely, without having an effect on the PARMOD™ chemistry involved in curing the metal particles to a continuous film. A charge director will create a different amount of charge on the same particles depending on the micellular properties of the charge director in the dispersing solvent. Therefore, different charge directors present in the same concentration will provide different amounts of charge. By varying the concentration of the charge director, the solution conductivity can be varied and the charge to mass ratio for the particles can be controlled. This is very important because the amount of charge on the particles and the amount of excess conductivity in the solution strongly affect the quality of the developed latent image and the ability to transfer a good quality image to another substrate. Enough of the charge director is used to obtain a preferred solution conductivity of between about 3 and about 100 pS/cm)

Surface active agents (surfactants) that have the properties described above can be used as charge directors. Examples of compounds which can be used as charge directors include alkali metal soaps, divalent and trivalent metal carboxylates (e.g., zirconium 2-ethylhexanoate, copper naphenate, or aluminum stearate), block copolymers, fatty amines (e.g., Troysol 98C), zwitterionic compounds (e.g., Lecithin), and sulphonated petroleum hydrocarbons *also known as metal petronates* (e.g., Basic Barium Petronate or Calcium Petronate), polymeric esters, phosphated diglycerides, sulfonates, functionalized diblock copolymers, and other ionic surfactant molecules.

Preferred charge directors include zirconium 2-ethylhexanoate, Troysol 98C, Lecithin, Basic Barium Petronate, and the Indigo Imaging agent, which is an n-vinyl pyrrolidine copolymer with lecithin and basic barium petronate integrated in the polymer and mixtures thereof. Preferred mixtures comprises lecithin and basic barium petronate in various ratios.

The dispersing solvent is a non-polar organic liquid with a vapor pressure such that it will evaporate relatively easily from the printed image, but not from the bulk liquid toner solution. The non-polar organic properties are necessary so that the solvent does not discharge the latent image as the toner particles develop it. The dispersing solvent acts as a carrier for the toner particles to get them to the latent image, but does not play a role in the

PARMODTM chemistry to form the continuous metal film. As with conventional liquid toners, once the desired image is formed, the dispersing solvent is removed by evaporation. Acceptable dispersing solvents include isoparaffinic hydrocarbons, halogenated or partially halogenated fluids and silicones. Some commercially available hydrocarbons include Isopar®, Norpar®, Shell-Sol®, and Soltrol®. The Isopar® series of isoparaffin solvents from Exxon Chemical are preferred as dispersing solvents, but other solvents with a resistivity greater than 10^{11} Ω -cm, a dielectric constant less than 3.5 and a boiling point in the range of 150 -220°C, can also be used. The Kauri-butanol number (solvency) should be less than 30.

The photopolymer material, such as a dry film or liquid resist, typically is formed of polymers which become cross-linked to form the imaged areas having electrical resistivity that can be an order of magnitude greater than the background or unexposed areas. The desired electrostatic latent image pattern remains in the photopolymer material by using the material's ability to retain differences in resistivity for relatively long periods of time after having been exposed to actinic radiation to form cross-linked areas of increased resistivity and areas unexposed to the actinic radiation which remain the less resistive areas.

A substrate is coated with a photopolymer material on at least one side. Exposure to actinic radiation causes cross-linking of the polymers in the material. The cross-linked photopolymer material exhibits a change in resistivity. A permanent latent image can be formed on the photopolymer material by actinically radiating the photopolymer through a mask or phototool or by drawing the desired pattern on the photopolymer with a laser. Both methods cross-link the irradiated photopolymer resulting in differences in the resistivity between imaged and non-imaged areas on the photopolymer material. The imaged photopolymer surface is then charged with a corona charging device to produce a pattern of charge retention that corresponds to the pattern of cross-linked photopolymer.

The charged photopolymer surface is then developed by the application of liquid metallic toner particles that are charged oppositely to the charge on the photopolymer surface. It may be necessary to wait a sufficient length of time after charging for the electric charge field to dissipate from above the unexposed/uncross-linked areas of the photopolymer

material before applying the toner particles. The charged liquid metallic toner particles are drawn to the charged areas of the photopolymer surface to form or develop the latent image.

The developed image thus is ready transfer to an electrically isolated conductive receiving surface or a nonconductive receiving surface, such as by a xeroprinting process where a master with the permanent image which is mounted to a grounded conductive backing, is charged, developed by the application of toner particles and the developed image is electrostatically transferred to another receiving surface to produce a circuit board with the desired conductive wiring pattern. This transfer method is more fully explained in, e.g., U.S. Patent No. 3,004,860 issued to Gundlach, herein specifically incorporated by reference in pertinent part.

In another preferred embodiment the charged image is created using ionography, in which the charged image is created by digitally controlled discharge from a row of electrodes. The image is toned with the liquid metallic toners described above and then thermally cured on a polymer substrate.

The examples described below indicate how the individual constituents of the preferred compositions and the conditions for applying them function to provide the desired result. The examples will serve to further typify the nature of this invention, but should not be construed as a limitation in the scope thereof, which scope is defined solely in the appended claims.

Example 1: Preparation of coated particles

A. Oleate coated silver nanopowder

An oleate coated silver powder was synthesized as follows: Silver oxalate (doped with 1% copper for heat stabilization) (20 g) is slurried into oleic acid (250 mL) by stirring with a magnetic stir bar. The solution is then heated on a hot plate with stirring to 185°C for 90 minutes. The solution is then allowed to cool to room temperature and the dark gray precipitate settles to the bottom. The solvent is then carefully removed by pipette from the top of the precipitate. Then to remove the remaining solvent the precipitate is washed with 3x50 mL tetrahydrofuran (THF) by stirring the precipitate with the THF then allowing it to settle and then removing the THF by pipette from the top of the precipitate. The precipitate is

then washed 3x50 ml with Isopar H in the same manner. Finally, the wet precipitate is dispersed in Isopar H (80 g) and treated ultrasonically for 30 minutes. This method gives a dispersion of silver particles with approximately 10% Ag (wt/wt).

B. Degussa silver flake coated with carboxylic acid(s)

Degussa silver flake (2g) was stirred together with oleic acid (0.1 g) in Isopar H (100 mL). The dispersion was ultrasonicated for 30 minutes. The oleic acid can be replaced with neodecanoic acid, noeheptanoic acid, neopentanoic acid, or 2-ethylhexanoic acid.

Example 2: Dispersion and charging of the coated particles

A. Oleate coated silver nanopowder toner.

The coated silver nanopowder from Example 1A (2 g) was ultrasonically dispersed in Isopar H (100 mL) for 30 minutes. To this dispersion was added enough Indigo Imaging Agent (IIA) to give a solution conductivity (as measured with a Scientifica 627 Conductivity Meter) of 2.7 pmho/cm.

B. Oleate coated silver nanopowder toner.

The coated silver nanopowder from Example 1A (2 g) was ultrasonically dispersed in Isopar H (100 mL) for 30 minutes. To this dispersion was added enough Troy Sol 98c (fatty amine) to give a solution conductivity of 0.7 pmho/cm.

C. Degussa silver flake toner.

Degussa silver flake (2 g) coated with oleic acid was ultrasonically dispersed in Isopar H (100 mL) for 30 minutes. To this dispersion was added enough Troy Sol 98c to give a solution conductivity of 0.7 pmho/cm.

D. Degussa silver flake toner.

Degussa silver flake (2 g) coated with neodecanoic acid was ultrasonically dispersed in Isopar H (100 mL) for 30 minutes. To this dispersion was added enough IIA to give a solution conductivity of 7.0 pmho/cm.

Example 3: Developing and converting electrostatic images to pure silver

A. Photopolymer substrate

A grounded, photoimaged printing plate with a liquid photo resistant surface was electrostatically charged by passing a 5000 V corona over it. Liquid toner from Example 2A was then applied to the printing plate to develop the latent electrostatic image. The image was then washed with Isopar H to remove excess toner. The image was then allowed to dry at room temperature (5 minutes). The developed image was then heated to 220°C for 3 minutes to give a continuous, pure silver film. The electrical resistivity of the silver film was 5.7 $\mu\Omega$ -cm compared with 1.59 $\mu\Omega$ -cm for bulk silver. The silver film had good adhesion to the substrate. The adhesion of the silver to the substrate was determined by a Scotch tape test where the tape was applied to the conductor and peeled off. This exerts a peel force on the conductor of approximately 6 lb/in (1050 N/m).

B. Dry film solder mask substrate

The same printing process as Example 3A was used except that the printing plate had dry film solder mask on the surface. The developed and dried silver toner image was then heated to 260°C for 3 minutes to give a continuous, pure silver film. The electrical resistivity of the silver film was 5.0 $\mu\Omega$ -cm with good adhesion to the substrate.

Example 4: Transferred and cured printed images

A. Corning 7059 low alkali glass substrate

Printing of an electrostatic image was done as in Example 3A and the developed image was washed with Isopar H. Rather than drying the image, the image was then transferred across a 1 mil, Isopar H filled gap, to a Corning 7059 low alkali glass substrate. The transfer was done by creating a 1 mil gap with spacers on the surface of the printed image. The gap was filled with Isopar H and the glass substrate was placed on the spacers. A corona with a voltage of 1250 V was then passed over the substrate. The electrostatic charge of the corona caused the toner particles on the developed image to move across the 1 mil gap and deposit on the glass substrate. The glass was then carefully removed and allowed to dry at room temperature. The transferred image was then heated to 400°C for 5 minutes to give a continuous, pure silver film. The electrical resistivity of sample was 1.7 $\mu\Omega$ -cm with good adhesion to the substrate. High resolution images with 40 μm wide lines and 80 μm wide spaces could be obtained.

B. Kapton®H flexible substrate

With a flexible substrate, the gap transfer method was varied. The DuPont Kapton® H flexible substrate was taped to a conductive aluminum, 4 inch diameter roller. The 1 mil gap was created with spacers and filled with Isopar H as in Example 4A. The roller with the Kapton®H substrate was then placed on the spacers and a transfer voltage of 1250 V was applied to the roller. The substrate was then rolled across the image. The developed image was transferred to the Kapton®H substrate. The substrate was then allowed to dry at room temperature (5 minutes) and removed from the roller. The image was heated to 350°C for 3 minutes to give a continuous, pure silver film. The electrical resistivity of the silver film was 4.5 $\mu\Omega$ -cm with good adhesion to the substrate.

While the initial application of this method may be to automobile rear lights, it is not limited to this application. All other automotive glass is a candidate for this technique including windshields, sidelights and mirrors. The invention can also be used in structures such as buildings and greenhouses.

Domestic mirrors, particularly those used in bathrooms, could benefit from this technique to provide a mist-free reflector with invisible, low voltage heater conductors applied to the front surface of the glass.

Yet other applications of this technique will be obvious to those skilled in the art.

Claim 1. A transparent substrate having deposited thereon a plurality of conductive metal traces, said conductive metal traces having a width of less than 25 micrometers.

Claim 2. The transparent substrate according to claim 1 wherein said substrate is selected from the group consisting of glass, polycarbonates, acrylic esters, polyesters, polyvinyl acetals, polyurethanes, and heat sensitive polymer substrates.

Claim 3. The transparent substrate according to claim 1 wherein said substrate is glass.

Claim 4. The transparent substrate according to claim 1 wherein said substrate is a polymer.

Claim 5. The transparent substrate according to claim 1, further comprising a first and a second laminate substrate, wherein said transparent substrate is interposed between said first and second laminate substrates.

Claim 6. The transparent substrate according to claim 5 wherein said first and second laminate substrates are glass.

Claim 7. The transparent substrate according to claim 5 wherein said first and second laminate substrates are plastic

Claim 8. The transparent substrate according to claim 5 wherein said first and second laminate substrates are polycarbonate.

Claim 9. The transparent substrate according to claim 1 wherein said plurality of traces are deposited in a pattern of parallel lines.

Claim 10. The transparent substrate according to claim 1 wherein said plurality of traces are deposited in a pattern of interconnected lines.

Claim 11. The transparent substrate according to claim 1 wherein said plurality of traces are deposited in a grid pattern.

Claim 12. The transparent substrate according to claim 1 wherein said plurality of traces are deposited in a hexagonal mesh pattern.

Claim 13. The transparent substrate according to claim 1 wherein said plurality of traces are deposited using a method selected from the group consisting of screen printing, stenciling, gravure printing, pad printing, flexographic printing, offset printing, electrostatic printing and ink jet printing.

Claim 14. The transparent substrate according to claim 1 wherein said plurality of traces are deposited using electrostatic printing.

Claim 15. A method for producing an electrically heatable transparent substrate which comprises the steps of:

A.) depositing on said substrate a plurality of traces, said traces being comprised of a mixture of metal particles and metallo-organic decomposition compound; and,

B.) heating said substrate to a temperature less than about 400 °C to cure said traces to metal.

Claim 16. The method of claim 15 wherein said plurality of traces have a width less than about 25 micrometers.

Claim 17. The method of claim 15 wherein said metal particles are selected from the group consisting of copper, silver, gold, zinc, cadmium, palladium, iridium, ruthenium, osmium, rhodium, platinum, iron, cobalt, and nickel, (Groups Ib, IIb, and VIII), and manganese, indium, tin, antimony, lead, and bismuth.

Claim 18. A transparent electroconductive substrate comprising a non-electroconductive assembly element of transparent material selected from the group

consisting of glass, polycarbonates, acrylic esters, polyesters, polyvinyl acetals and polyurethanes; an electroconductive circuit portion comprising lines of highly conductive metal carried by said transparent element; and means for electrically connecting said lines to a source of electricity.

Claim 19. The transparent electroconductive substrate of Claim 18, further comprising a second and third electroconductive assembly elements, wherein said electroconductive assembly element is laminated between said second and third electroconductive assembly elements.

Claim 20. The transparent electroconductive substrate of Claim 18, wherein said assembly element is selected from the group consisting of glass and plastic and said highly conductive metal is silver.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/27119

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B32B 3/00, 27/14; C25D 5/02

US CL :428/198, 210; 427/123

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/198, 200, 203, 204, 206, 208, or 210; 427/123

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| X,P | US 5,882,722 A (KYDD) 16 March 1999, see entire document. | 1-20 |
| X | US 5,246,764 A (LAPORTE et al) 21 September 1993, see entire document. | 1-14 |

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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| *P* document published prior to the international filing date but later than the priority date claimed | |

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28 FEBRUARY 2000

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B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

WEST

search terms: laminate, substrate, composite, glass, plastic, polycarbonate, transparent, acrylic ester, polyester, polyvinyl acetal, polyurethane, metal, trace, bond, strip, particle, copper, silver, gold, screen printing, stenciling, flexographic printing, ink jet printing